# 蘆筍罐頭脫錫研究
# （第二報）模擬裝罐試驗

## Model Test Studies on the Detinning of Canned Asparagus

張炳揚、愼錫泉、張爲憲

**P. Y. Chang　S. C. Shen　W. H. Chang**

### Summary

Model tests were carried out to study the factors which may affect the detinning of canned asparagus. Various organic acids and nitrate were added, alone or in combinations, to a sodium chloride solution at different *p*H's and the mixtures were canned. The cans were examined at intervals during storage at 45°C for 40 days. Among the acids tested, only citric or malic acid caused appreciable extent of initial detinning. Nitrate, though unable to cause detinning when present alone, accelerated later detinning if present together with citric or malic acid. Thus, it seems possible to divide detinning into two stages, *i.e.* "initial" detinning and "later" detinning. Mixed acids containing acetic or phytic acid, however, showed some retardation of detinning. When nitrate-containing solutions caused appreciable extent of detinning, nitrate concentrations decreased and *p*H values rose. When detinning was appreciable, whether nitrate was present or not, little iron was picked up. These results suggest that, in canned asparagus, citric and malic acids might be responsible for the initial detinning, and that the later detinning is probably accelerated by nitrate.

### Introduction

Asparagus is widely known as a strong detinner [1], and it has been reported that the amount of dissolved tin in canned asparagus after a certain period of storage may reach as high as 400 *ppm* [2~4], which is much higher than the presently allowable limit of 250 *ppm*. However, little work has been done on the detinning of canned asparagus, although there have been plenty of studies done on that of many other canned foods. In order to reduce the extent of detinning of canned asparagus, the uses of end-lacquered cans [1] and High Tin Fillet cans [2] have been recommended.

Many factors have been reported to be affecting the performances of tin-plate cans in a wide variety of food products. Important ones among them are nitrate, organic acids, and some plant pigments. Nitrate has been widely regarded as a detinning accelerator in various kinds of canned food products, including pumpkin [5], beets [5], mangold [6], green beans [7,8], tomatoes [8], spinach [9], Mandarin orange [10,11], orange juice [12], and tomato juice [13]; and the nitrate-accelerated detinning was further found to be closely related to the *p*H of the canned products [14,15]. Organic acids, according to Hartwell [16], influence detinning in very

complicated ways. Their effects may be positive or negative, depending upon the nature and the concentration of the acids, and also upon the nature of the foods. Citric and malic acids have often been mentioned to cause detinning. Among plant pigments, anthocyanins[16,17] have been reported to accelerate detinning. Recently, Japanese workers[18] reported, after a study with white asparagus containing relatively little nitrate, that besides nitrate and organic acids, some sulfur compounds which are rich in the tips may also be responsible for the detinning of canned asparagus.

Canning tests, in which different amounts of nitrate were added to canned foods to see the effects on detinning, showed that the detinning was accelerated by the nitrate added in canned Mandarin orange[10,11], and in canned orange juice especially when the *p*H was low[14,15]. In our previous experiment[19] with white asparagus containing about 40 *ppm* nitrate-N, however, the added nitrate did not show appreciable acceleration of detinning. Although canning tests of this kind have the advantage of taking into consideration all factors present in the raw materials, they bear two disadvantages at the same time. First, interpretation of the experimental results will be very difficult because complicated interactions may take place between too many factors, some of which are not even known. Second, the factor compounds to be tested may not be entirely absent in the raw materials, and the amounts of the endogenous factor compounds will naturally diminish the effects of the compounds added. Therefore, model tests are obviously more effective than canning tests in order to obtain fundamental informations about the effects of food components on detinning.

When Strodtz and Henry[7] canned 0.3% citrate buffers at different *p*H's from 3.0 to 6.0, the amounts of detinning after 15-days' storage at 130°*F* were little, independent of the *p*H. However, if 400 or 800 *ppm* nitrate was added, there occurred high extents of detinning dependent on both the *p*H and the nitrate concentration; *i.e.*, more detinning resulted from lower *p*H's and higher nitrate concentrations. Recently, Horio, *et al.*[20] carried out a similar model test simulating canned orange juice, in which 0.4% citrate buffers containing 10% sugar were canned at an acidic *p*H, 4.5—4.8. When no nitrate was added, both the initial detinning and the later detinning after 30-days' storage at 38°*C* were minute; but when 50 or 100 *ppm* nitrate-N was added, appreciable initial detinning and remarkable later detinning were observed. In our previous model test simulating canned asparagus[19], in which 2.2% NaCl solutions were adjusted to *p*H 6.2 with citric acid and canned with or without the addition of 25 *ppm* nitrate-N, little detinning was observed after 12-weeks' storage at 45°*C*. In another model test[21], in which 0.1*N* citrate buffers containing 1.2% NaCl were adjusted to different *p*H's from 3.4 to 6.4 and canned with the addition of 25 *ppm* nitrate-N, we found appreciable initial detinning at all *p*H's and marked later detinning at *p*H's lower than 5.4. The discrepancy between the results of initial detinning in our previous model tests might have arisen from the difference in amounts of citrate present in the brine; while the discrepancies between those of our experiment and other workers might be due to the presence of NaCl in our experiment. Therefore, the purpose of the present model tests is to look further into the effects of the addition of different amounts of various organic acids and nitrate, alone or in combinations, to a sodium chloride solution simulated to the brine of canned asparagus, on detinning at different *p*H's. Citric and malic acids were chosen because they have been



reported to be the major constituent acids in white[22] and green asparagus[23]. Acetic acid was added because it is an acid without chelating capability and is also present in white asparagus[22], while phytic acid was added because it is a chelating acid with anti-metal-corrosion activity.

## Experimental Methods

### Filling solutions

All filling solutions used in the model tests were based on a 1.2% NaCl solution to which different amounts of citric, malic, acetic or phytic acid and potassium nitrate were added, alone or in combinations, and the *p*H was adjusted with HCl or NaOH solution. The ingredients and *p*H values of the filling solutions are shown in the left half of the Table 2.

### Canning

Tin-plate cans used in the present experiments were all Taiwan No. 4 cans with both ends lacquered, supplied by the Kao-shiung Can Factory of Taiwan Pineapple Company. The characteristics of the cans are shown in Table 1.

Table 1. Characteristics of the tin-plate cans used.

| Characteristics | Value obtained* | Remarks |
|---|---|---|
| Tin coating weight | 1.18 *lb/b.b.* | The tin plate used for the cans was hot-dipped for the body and No. 100 for the ends. |
| Pickling lag value | 10 *sec.* | The qualified value is 10 *sec.* or below. |
| Enamel rater value | 80 *ma*/6.2*V* | |
| Iron solution value | 15 | The qualified value is 20 or below. |

* An average of the values obtained for 3 cans.

The procedures for preparing the model test cans were the same as those for canning asparagus. The solutions were filled into the cans, exhausted at 98°*C* for 10 *min.*, sealed, sterilized at 121°*C* for 16 *min.*, cooled, and then stored at 45°*C*.

### Examination

Since it has been found from our previous experiments[19,21] and others[7,20] that high-temperature storage at 45°*C* for 4 weeks is about long enough to observe the detinning effects in model tests in cans with both ends lacquered, examination of the test cans in the present studies was scheduled at 1, 7, 14, 28 and 40 days of storage at 45°*C*. For each test item at every time of examination, 4 cans were opened and the contents mixed together, from which two samples were taken for the determination of *p*H, titratable acidity, nitrate-N (if nitrate was added), and dissolved tin. Dissolved tin was determined by the iodometric method recommended by NCA of the United States[24], and nitrate-N was determined by titrating the ammonia derived on reduction and distillation[25]. Dissolved iron was determined, only after 40-days' storage, by atomic absorption spectrophotometry.

Table 2. Composition of filling solution#, and the degrees of detinning and iron pick-up during 40-days' storage at 45°C.

| Expt. No. | Code | Citric acid(N) | Malic acid(N) | Acetic acid(N) | Phytic acid(N) | Nitrate-N (ppm) | pH | Iron** pick-up (ppm) | Detinning*** Initial | Detinning*** Later |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | B | — | — | — | — | — | 5.4 | 40.1 | — | — |
| 2* | C-0.01 | 0.01 | — | — | — | — | 5.4 | 2.4 | ⫴ | ± |
| 3 | C-0.02 | 0.02 | — | — | — | — | 5.4 | 1.2 | ⫴ | ± |
| 4 | C-0.1 | 0.1 | — | — | — | — | 5.4 | 1.4 | ⫲ | ± |
| 5* | M-0.01 | — | 0.01 | — | — | — | 5.4 | 8.3 | + | ± |
| 6 | M-0.1 | — | 0.1 | — | — | — | 5.4 | 1.9 | ⫲ | ± |
| 7* | A-0.002 | — | — | 0.002 | — | — | 5.4 | 42.1 | — | — |
| 8 | A-0.02 | — | — | 0.02 | — | — | 5.4 | 53.1 | — | — |
| 9* | CMA | 0.01 | 0.01 | 0.002 | — | — | 5.4 | 1.5 | ⫴ | ± |
| 10* | P-0.01 | — | — | — | 0.01 | — | 5.4 | 4.9 | — | — |
| 11 | P-0.05 | — | — | — | 0.05 | — | 5.4 | 7.0 | — | ± |
| 12 | C-4.4 | 0.01 | — | — | — | — | 4.4 | 2.8 | ⫴ | ± |
| 13* | C-5.4 | 0.01 | — | — | — | — | 5.4 | 2.4 | ⫴ | ± |
| 14 | C-6.4 | 0.01 | — | — | — | — | 6.4 | 1.9 | + | ± |
| 15 | M-4.4 | — | 0.01 | — | — | — | 4.4 | 1.2 | ⫲ | ± |
| 16* | M-5.4 | — | 0.01 | — | — | — | 5.4 | 8.3 | + | ± |
| 17 | M-6.4 | — | 0.01 | — | — | — | 6.4 | 20.4 | — | ± |
| 18 | A-4.4 | — | — | 0.002 | — | — | 4.4 | 61.3 | — | — |
| 19* | A-5.4 | — | — | 0.002 | — | — | 5.4 | 42.1 | — | — |
| 20 | A-6.4 | — | — | 0.002 | — | — | 6.4 | 33.1 | — | — |
| 21 | P-4.4 | — | — | — | 0.01 | — | 4.4 | 5.1 | — | — |
| 22* | P-5.4 | — | — | — | 0.01 | — | 5.4 | 4.9 | — | — |
| 23 | P-6.4 | — | — | — | 0.01 | — | 6.4 | 2.4 | — | — |
| 24 | N-20 | — | — | — | — | 20 | 5.4 | 58.9 | — | — |
| 25* | N-40 | — | — | — | — | 40 | 5.4 | 48.0 | — | — |
| 26 | N-100 | — | — | — | — | 100 | 5.4 | 48.9 | — | — |
| 27* | N-0C | 0.01 | — | — | — | 0 | 5.4 | 2.4 | ⫴ | ± |
| 28 | N-20C | 0.01 | — | — | — | 20 | 5.4 | 2.9 | ⫴ | + |
| 29* | N-40C | 0.01 | — | — | — | 40 | 5.4 | 2.4 | ⫴ | ⫲ |
| 30 | N-100C | 0.01 | — | — | — | 100 | 5.4 | 1.5 | ⫴ | ⫲ |
| 31* | N-0A | — | — | 0.002 | — | 0 | 5.4 | 42.1 | — | — |
| 32 | N-20A | — | — | 0.002 | — | 20 | 5.4 | 40.1 | — | — |
| 33* | N-40A | — | — | 0.002 | — | 40 | 5.4 | 34.1 | — | — |
| 34 | N-100A | — | — | 0.002 | — | 100 | 5.4 | 35.9 | — | — |
| 35* | N-0CMA | 0.01 | 0.01 | 0.002 | — | 0 | 5.4 | 1.5 | ⫲ | ± |
| 36 | N-20CMA | 0.01 | 0.01 | 0.002 | — | 20 | 5.4 | 2.0 | ⫲ | + |
| 37* | N-40CMA | 0.01 | 0.01 | 0.002 | — | 40 | 5.4 | 1.9 | ⫲ | + |
| 38 | N-100CMA | 0.01 | 0.01 | 0.002 | — | 100 | 5.4 | 2.0 | ⫲ | ⫲ |
| 39 | N-3.4 | — | — | — | — | 40 | 3.4 | 57.2 | — | ± |
| 40 | N-4.4 | — | — | — | — | 40 | 4.4 | 41.3 | — | — |
| 41 | N-4.9 | — | — | — | — | 40 | 4.9 | 34.1 | — | — |
| 42* | N-5.4 | — | — | — | — | 40 | 5.4 | 48.0 | — | — |
| 43 | N-6.4 | — | — | — | — | 40 | 6.4 | 29.0 | — | — |
| 44 | NC-3.4 | 0.01 | — | — | — | 40 | 3.4 | 3.1 | ⫼ | ⫼ |
| 45 | NC-4.4 | 0.01 | — | — | — | 40 | 4.4 | 3.4 | ⫼ | ⫼ |
| 46 | NC-4.9 | 0.01 | — | — | — | 40 | 4.9 | 2.6 | ⫼ | ⫴ |
| 47* | NC-5.4 | 0.01 | — | — | — | 40 | 5.4 | 2.4 | ⫴ | ⫲ |
| 48 | NC-6.4 | 0.01 | — | — | — | 40 | 6.4 | 1.4 | ⫲ | + |
| 49 | NA-3.4 | — | — | 0.002 | — | 40 | 3.4 | 29.2 | — | — |
| 50 | NA-4.4 | — | — | 0.002 | — | 40 | 4.4 | 56.1 | — | — |
| 51 | NA-4.9 | — | — | 0.002 | — | 40 | 4.9 | 56.1 | — | — |
| 52* | NA-5.4 | — | — | 0.002 | — | 40 | 5.4 | 34.1 | — | — |
| 53 | NA-6.4 | — | — | 0.002 | — | 40 | 6.4 | 29.0 | — | — |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 54 | NCMA-3.4 | 0.01 | 0.01 | 0.002 | — | 40 | 3.4 | 4.9 | ### | ### |
| 55 | NCMA-4.4 | 0.01 | 0.01 | 0.002 | — | 40 | 4.4 | 2.2 | ### | ### |
| 56 | NCMA-4.9 | 0.01 | 0.01 | 0.002 | — | 40 | 4.9 | 2.4 | ### | ## |
| 57* | NCMA-5.4 | 0.01 | 0.01 | 0.002 | — | 40 | 5.4 | 1.9 | ## | + |
| 58 | NCMA-6.4 | 0.01 | 0.01 | 0.002 | — | 40 | 6.4 | 2.0 | + | ± |
| 59 | NP-3.4 | — | — | — | 0.01 | 40 | 3.4 | 9.1 | — | — |
| 60 | NP-4.4 | — | — | — | 0.01 | 40 | 4.4 | 4.9 | — | — |
| 61 | NP-4.9 | — | — | — | 0.01 | 40 | 4.9 | 5.5 | — | — |
| 62* | NP-5.4 | — | — | — | 0.01 | 40 | 5.4 | 5.0 | — | — |
| 63 | NP-6.4 | — | — | — | 0.01 | 40 | 6.4 | 2.9 | — | — |
| 64* | NC-0 | 0 | — | — | — | 40 | 5.4 | 48.0 | — | — |
| 65* | NC-0.01 | 0.01 | — | — | — | 40 | 5.4 | 2.4 | ### | ## |
| 66 | NC-0.02 | 0.02 | — | — | — | 40 | 5.4 | 1.4 | ### | ## |
| 67 | NC-0.1 | 0.1 | — | — | — | 40 | 5.4 | 2.0 | ### | + |
| 68* | NA-0 | — | — | 0 | — | 40 | 5.4 | 48.0 | — | — |
| 69* | NA-0.002 | — | — | 0.002 | — | 40 | 5.4 | 34.1 | — | — |
| 70 | NA-0.02 | — | — | 0.02 | — | 40 | 5.4 | 50.4 | — | — |
| 71* | NP-0 | — | — | — | 0 | 40 | 5.4 | 48.0 | — | — |
| 72* | NP-0.01 | — | — | — | 0.01 | 40 | 5.4 | 5.0 | — | — |
| 73 | NP-0.05 | — | — | — | 0.05 | 40 | 5.4 | 9.1 | ± | + |
| 74* | NCMAP-0 | 0.01 | 0.01 | 0.002 | 0 | 40 | 5.4 | 1.9 | ## | + |
| 75 | NCMAP-0.01 | 0.01 | 0.01 | 0.002 | 0.01 | 40 | 5.4 | 2.0 | + | + |
| 76 | NCMAP-0.05 | 0.01 | 0.01 | 0.002 | 0.05 | 40 | 5.4 | 4.2 | + | ## |

# All of the filling solutions are based on a 1.2% NaCl solution.

* Experiment Nos. 2 (C-0.01), 13 (C-5.4) and 27 (N-0C) are entirely the same, but are repeatedly listed with different codes merely for the convenience of comparison. The same applies to the following groups: Nos. 5 (M-0.01) and 16 (M-5.4); Nos. 7 (A-0.002), 19 (A-5.4) and 31 (N-0A); Nos. 9 (CMA) and 35 (N-0CMA); Nos. 10 (P-0.01) and 22 (P-5.4); Nos. 25 (N-40), 42 (N-5.4), 64 (NC-0), 68 (NA-0) and 71 (NP-0); Nos. 29 (N-40C), 47 (NC-5.4) and 65 (NC-0.01); Nos. 33 (N-40A), 52 (NA-5.4) and 69 (NA-0.002); Nos. 37 (N-40CMA). 57 (NCMA-5.4) and 74 (NCMAP-0); and Nos. 62 (NP-5.4) and 72 (NP-0.01).

** The amounts of iron pick-up were measured after 40-days' storage at 45°C.

*** "Initial detinning" indicates the rapid rise in dissolved tin during the rather early stage of storage. It does not accompany a continuous increase in dissolved tin, which is called "later detinning".



## Results

### Comparison of detinning and iron pick-up

In Table 2, the ingredients and the *p*H's of the filling solutions used in all of the experiments are listed on the left half, and on the right half are listed the extents of detinning, which was divided into "initial" and "later" detinning and expressed with the use of plus and minus signs, together with the amounts of iron pick-up measured after 40-days' storage at 45°C. The results can be summarized as follows:

(a) Citric acid was the most effective in causing the initial detinning, and was effective at the concentrations (Expt. Nos. 2-4) and the *p*H's (Expt. Nos. 12-14) tested; while malic acid was not only less effective, but was effective only at higher concentrations (Expt. Nos. 5, 6) or at lower *p*H's (Expt. Nos. 15-17).

(b) Nitrate itself could not cause initial detinning at the concentrations (Expt. Nos. 24-26) and the *p*H's (Expt. Nos. 39-43) tested, but accelerated the later detinning effectively if the initial detinning was caused by citric or malic acid (Expt. Nos. 27-30, 44-48). And if there was no initial detinning, the co-existence of nitrate was still unable to cause detinning (Expt. Nos. 31-34, 49-53).

(c) Acetic and phytic acids were not only ineffective as a detinning initiator (Expt. Nos. 7, 8, 10, 11, 18-21), but were even likely to retard both initial and later detinning to some extent, because the mixed acids in the presence of nitrate resulted in less detinning than when only citric acid was present (Expt. Nos. 35-38, 54-58), and because the presence of phytic acid in the mixed acids completely inhibited the initial detinning for a certain period of storage (Expt. Nos. 74-76).

(d) Appreciable detinning always resulted in little iron pick-up regardless of the presence of nitrate, and iron pick-up was appreciable only when detinning was minute, as in the blank test and in the cases when only acetic acid or nitrate was present (Expt. Nos. 7, 8, 18-20, 24-26, 31-34, 39-43, 49-53). In this connection, phytic acid showed a peculiar effect that gave neither iron pick-up nor appreciable detinning for quite a long period of storage (Expt. Nos. 10, 11, 21-23, 59-63, 71-73)

For all the cases of appreciable detinning, the mode of detinning was further described below with graphic illustrations.

### Effects of different acids on detinning

The effects of citric, malic or phytic acid alone at different concentrations, as well as that of the mixed acids on detinning are shown in Fig. 1. Acetic acid was not included because it did not cause appreciable detinning. Citric acid at the concentration range tested, caused about the same degree of detinning. Although the detinning was very fast and appreciable, it did not continue to any extent, resulting in a steep rise on a progress curve followed by a plateau, which is the most typical characteristic of the "initial detinning" as we call.

Malic acid also caused the same type of detinning, although not as effective and distinct as citric acid. The mixed acids did not give more initial detinning than citric acid alone, and phytic acid caused slight detinning only after a certain period of high-temperature

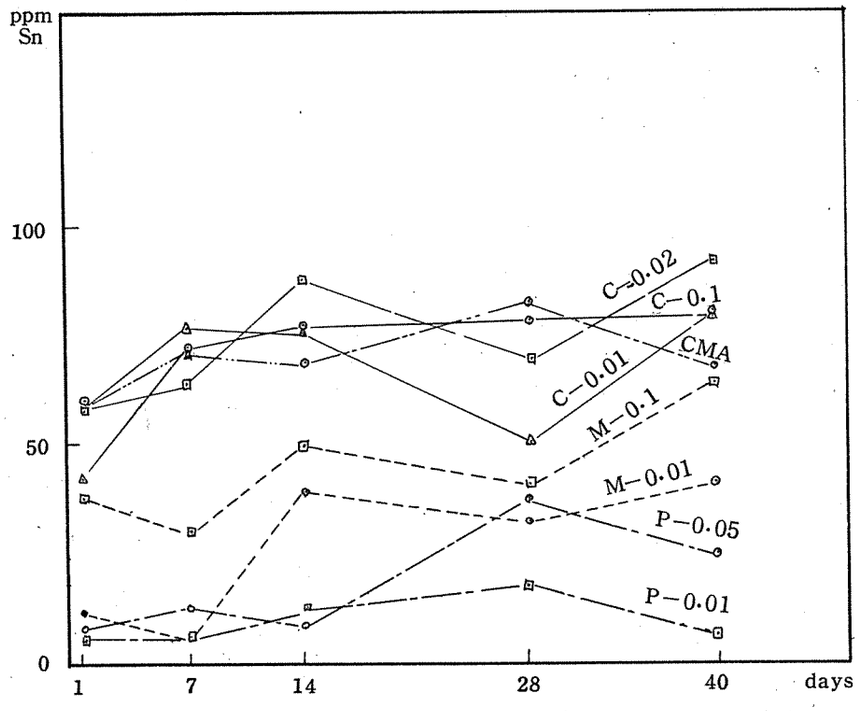


Fig. 1. Effects of different acids at different concentrations on detinning.

storage.

The effects of *p*H on the initial detinning caused by citric or malic acid alone are shown in Fig. 2. Acetic and phytic acids were not included because they did not cause appreciable initial detinning at any *p*H tested. Although more initial detinning was observed at lower *p*H's for both citric and malic acids, the trends that the detinning does not contiune and that citric acid is more effective than malic acid, were still observed at all *p*H's tested.

Acceleration of detinning by nitrate in the presence of different acids

Although nitrate alone could not cause detinning at any *p*H tested, its co-existence with acids which can cause initial detinning, such as citric or the mixed acids, resulted in remarkable acceleration of the " later detinning " as we call ( Fig. 3). The " later detinning " is different from the " initial detinning " in the fact that the fast initial detinning caused by acids was followed by different degrees of continuous detinning depending upon the amounts of nitrate present. It can be seen from Fig. 3 that the acceleration of the later detinning by nitrate was more remarkable when the initial detinning was caused by citric acid alone than by the mixed acids. The same tendency was also observed in the experiments on the effects of *p*H on the nitrate-accelerated later detinning, only except for *p*H3.4 where the relationship was reversed ( Fig. 4 ). Fig. 4 also shows that the acceleration of later detinning by nitrate was more remarkable at lower *p*H's.

Although the initial detinning caused by citric acid was almost independent of the acid



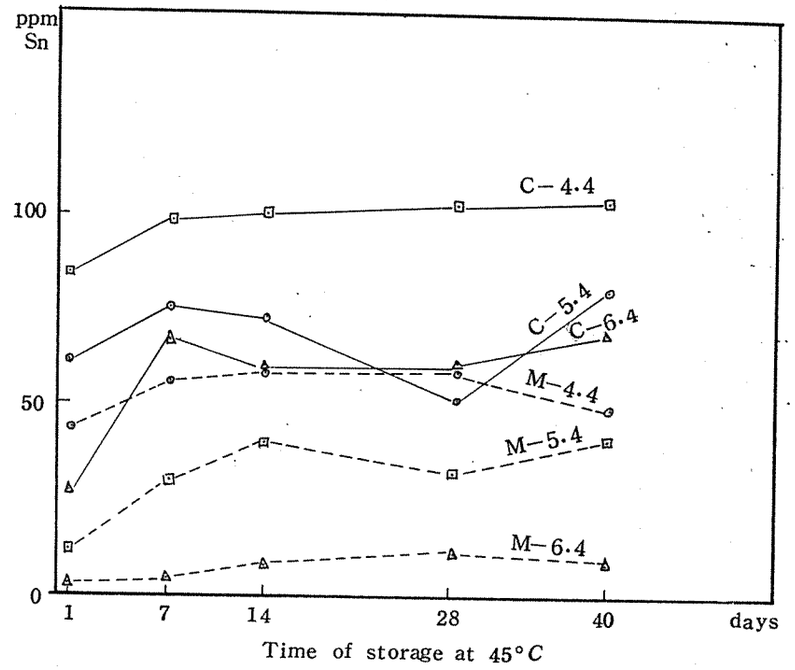


Fig. 2. Effects of *p*H on the detinning caused by citric and malic acids.

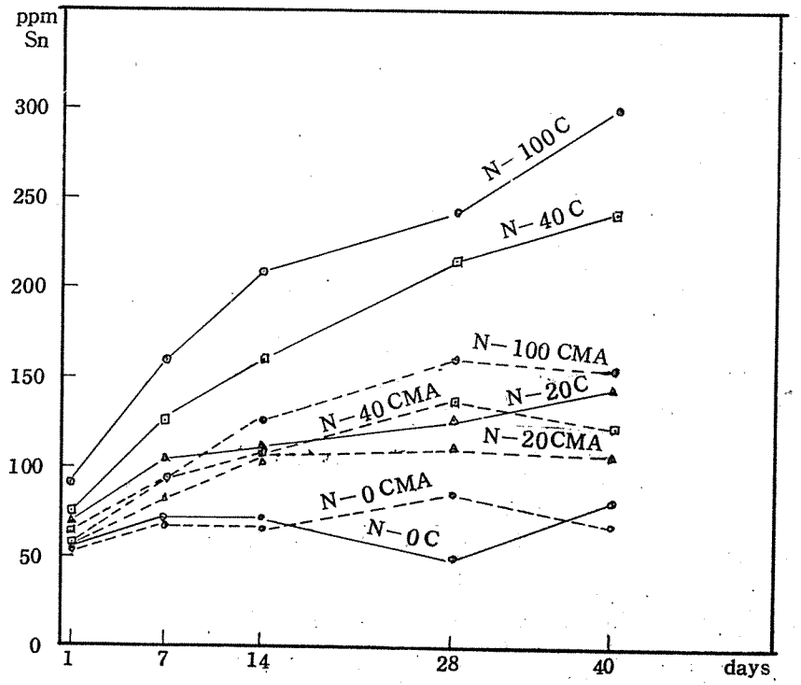


Fig. 3. Acceleration of detinning by nitrate in the presence of citric and the mixed acids.

concentration (Fig. 1), the nitrate-accelerated later detinning in the presence of citric acid was inversely related to the acid concentration (Fig. 5), which brings about more complications to the detinning phenomena. Fig. 5 also shows that the slight detinning caused by a high concentration of phytic acid (Fig. 1) was not accelerated by nitrate at all. Furthermore, Fig. 6 indicates that the presence of phytic acid in the mixed acids inhibited the initial detinning for a certain period of storage, but not forever.

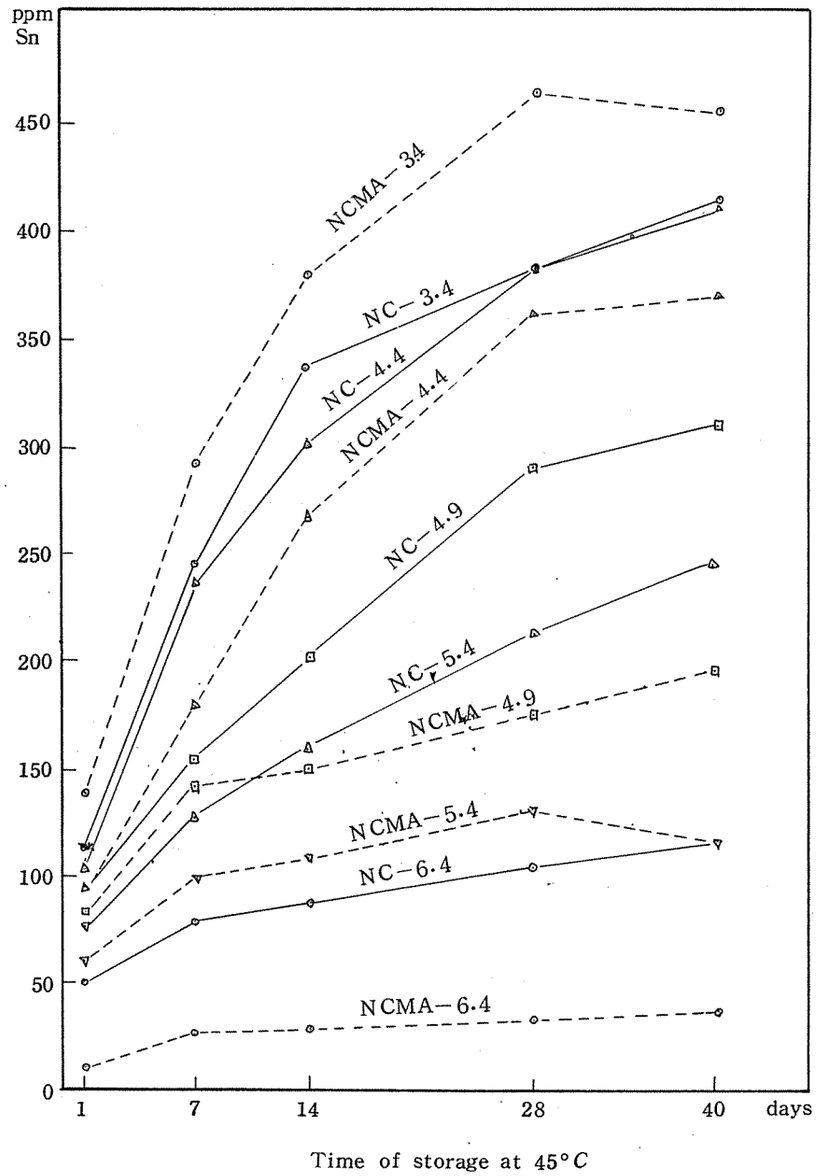


Fig. 4. Effects of *p*H on the nitrate-accelerated detinning in the presence of citric and the mixed acids.



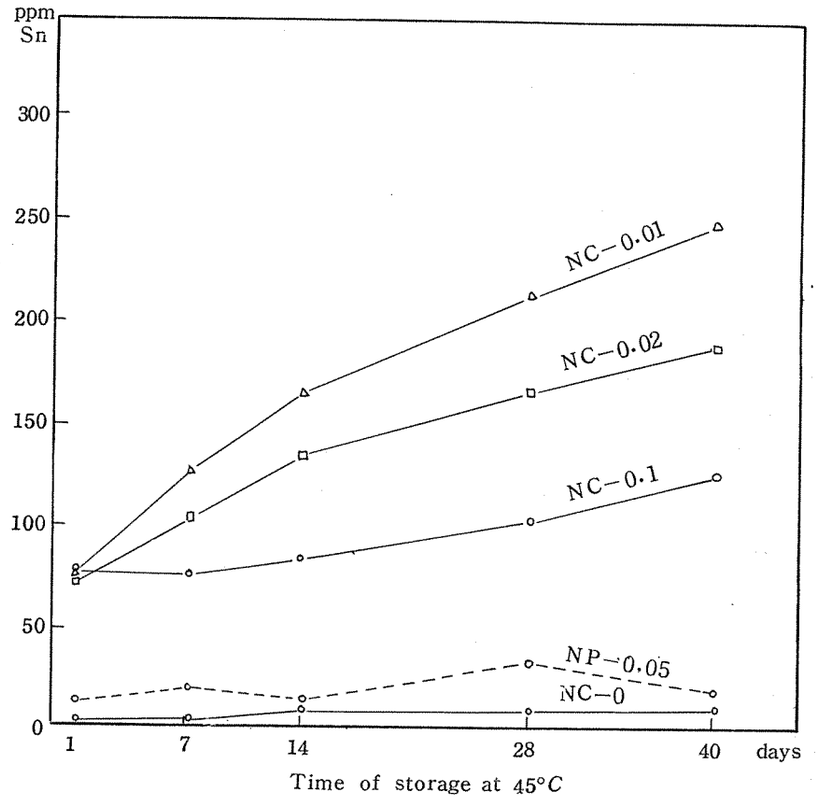


Fig. 5. Effects of citric and phytic acids concentrations on the nitrate-accelerated detinning.

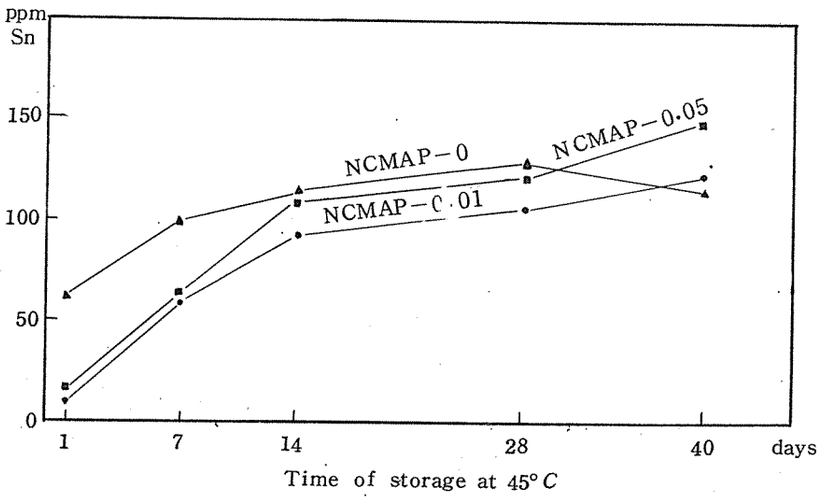


Fig. 6. Effects of phytic acid on the detinning caused by the mixed acids and nitrate.

Table 3. Correlation between detinning and the changes in nitrate concentrations in model tests during storage at 45° *C* for 40 days.

| Expt. No. | Code | Original nitrate-N (*ppm*) | Original *p*H | Final dissolved tin(*ppm*) | Final nitrate-N (*ppm*) | Nitrate-N disappeared (*ppm*) |
|---|---|---|---|---|---|---|
| 24 | N-20 | 20 | 5.4 | 14.9 | 19.0 | 1.0 |
| 25 | N-40 | 40 | 5.4 | 8.6 | 39.5 | 0.5 |
| 26 | N-100 | 100 | 5.4 | 14.2 | 100.2 | — |
| 28 | N-20C | 20 | 5.4 | 160.3 | 7.8 | 12.2 |
| 29 | N-40C | 40 | 5.4 | 251.1 | 18.3 | 21.7 |
| 30 | N-100C | 100 | 5.4 | 297.4 | 34.2 | 65.8 |
| 32 | N-20A | 20 | 5.4 | 4.5 | 16.4 | 3.6 |
| 33 | N-40A | 40 | 5.4 | 3.6 | 38.9 | 1.1 |
| 34 | N-100A | 100 | 5.4 | 6.0 | 93.4 | 6.6 |
| 36 | N-20CMA | 20 | 5.4 | 109.0 | 8.4 | 11.6 |
| 37 | N-40CMA | 40 | 5.4 | 125.0 | 18.3 | 21.7 |
| 38 | N-100CMA | 100 | 5.4 | 160.3 | 50.1 | 49.9 |
| 39 | N-3.4 | 40 | 3.4 | 25.0 | 39.0 | 1.0 |
| 40 | N-4.4 | 40 | 4.4 | 7.5 | 38.9 | 1.1 |
| 41 | N-4.9 | 40 | 4.9 | 11.6 | 37.8 | 2.2 |
| 42 | N-5.4 | 40 | 5.4 | 8.6 | 39.5 | 0.5 |
| 43 | N-6.4 | 40 | 6.4 | 6.7 | 39.4 | 0.6 |
| 44 | NC-3.4 | 40 | 3.4 | 419.0 | 15.6 | 24.4 |
| 45 | NC-4.4 | 40 | 4.4 | 417.3 | 9.2 | 30.8 |
| 46 | NC-4.9 | 40 | 4.9 | 319.4 | 16.4 | 23.6 |
| 47 | NC-5.4 | 40 | 5.4 | 251.1 | 18.3 | 21.7 |
| 48 | NC-6.4 | 40 | 6.4 | 124.8 | 16.9 | 23.1 |
| 49 | NA-3.4 | 40 | 3.4 | 17.6 | 37.4 | 2.6 |
| 50 | NA-4.4 | 40 | 4.4 | 5.5 | 37.9 | 2.1 |
| 51 | NA-4.9 | 40 | 4.9 | 4.6 | 37.6 | 2.4 |
| 52 | NA-5.4 | 40 | 5.4 | 3.6 | 38.9 | 1.1 |
| 53 | NA-6.4 | 40 | 6.4 | 2.5 | 37.2 | 2.8 |
| 54 | NCMA-3.4 | 40 | 3.4 | 458.9 | 10.1 | 29.9 |
| 55 | NCMA-4.4 | 40 | 4.4 | 375.2 | 11.8 | 28.2 |
| 56 | NCMA-4.9 | 40 | 4.9 | 213.4 | 21.1 | 18.9 |
| 57 | NCMA-5.4 | 40 | 5.4 | 125.0 | 18.3 | 21.7 |
| 58 | NCMA-6.4 | 40 | 6.4 | 37.5 | 30.7 | 9.3 |
| 59 | NP-3.4 | 40 | 3.4 | 4.2 | 35.9 | 4.1 |
| 60 | NP-4.4 | 40 | 4.4 | 4.7 | 36.4 | 3.6 |
| 61 | NP-4.9 | 40 | 4.9 | 3.3 | 34.6 | 5.4 |
| 62 | NP-5.4 | 40 | 5.4 | 0.5 | 37.1 | 2.9 |
| 63 | NP-6.4 | 40 | 6.4 | 3.6 | 37.0 | 3.0 |



Table 3. Correlation between detinning and the changes in nitrate concentrations in model tests during storage at 45° *C* for 40 days. (Continued)

| Expt. No. | Code | Original nitrate-N (*ppm*) | Original *p*H | Final dissolved tin(*ppm*) | Final nitrate-N (*ppm*) | Nitrate-N disappeared (*ppm*) |
|---|---|---|---|---|---|---|
| 64 | NC-0 | 40 | 5.4 | 8.6 | 39.5 | 0.5 |
| 65 | NC-0.01 | 40 | 5.4 | 251.0 | 18.3 | 21.7 |
| 66 | NC-0.02 | 40 | 5.4 | 195.3 | 23.5 | 16.5 |
| 67 | NC-0.1 | 40 | 5.4 | 134.5 | 28.6 | 11.4 |
| 69 | NA-0.002 | 40 | 5.4 | 3.6 | 38.9 | 1.1 |
| 70 | NA-0.02 | 40 | 5.4 | 8.4 | 35.2 | 4.8 |
| 72 | NP-0.01 | 40 | 5.4 | 0.5 | 37.1 | 2.9 |
| 73 | NP-0.05 | 40 | 5.4 | 20.8 | 7.3 | 32.7 |
| 74 | NCMAP-0 | 40 | 5.4 | 125.0 | 18.3 | 21.7 |
| 75 | NCMAP-0.01 | 40 | 5.4 | 132.3 | 10.2 | 29.8 |
| 76 | NCMAP-0.05 | 40 | 5.4 | 155.9 | 5.0 | 35.0 |

Changes of *p*H, acidity and nitrate concentration

Although the changes in *p*H of the model test solutions during storage were somewhat irregular, in most cases *p*H values increased steadily and titratable acidity decreased simultaneously. The changes in nitrate concentration, when nitrate was added to the filling solutions, are shown in Table 3. The correlation between the extent of detinning and the decrease in nitrate concentration was rather clear-cut. When the later detinning was remarkable due to the presence of nitrate, as in the cases of citric acid-nitrate and the mixed acids-nitrate combinations, the nitrate concentration decreased steadily as the later detinning went on, although no proportional relationship between the extent of detinning and the decrease in nitrate concentration was observed. Contrarily, when detinning was not significant, there was little decrease in nitrate concentration. The only exception was observed in the phytic acid nitrate combination (NP-0.05), in which a remarkable decrease in nitrate concentration was observed in spite of the fact that there was neither appreciable detinning nor iron pick-up.

## Discussion and Conclusion

Initial detinning caused by acids

It has long been known that in the corrosion of canned-acid products, tin is anodic to iron. This phenomenon is attributed to the high hydrogen overvoltage of the tin electrode[26], to the ability of stannous ion to form stable complexes with many food components, such as citrate, chloride, and hydroxyl, *etc.*[27,28], or to the effect of stannous ion in raising the cathodic polarization on iron[29,30]. In the present studies, citric and malic acids which make tin anodic to iron, caused appreciable initial detinning with negligible iron pick-up. The initial detinning was fast, but did not continue because of the lack of suitable depolarizers. The facts that the model tests made by Strodtz and Henry[7] and by Horio, *et al.*[20] with

citrate buffers resulted in negligible detinning in the absence of nitrate, are probably due to the absence of NaCl in their test solutions. On the other hand, acetic acid caused iron pick-up instead of detinning, because it makes iron anodic to tin[29]. It seems noteworthy that the NaCl solution itself also makes iron anodic to tin, so that there was an appreciable amount of iron pick-up in the blank test. Phytic acid, which possesses the capability of both metal-chelation and anti-metal-corrosion, showed a rather peculiar effect, resulting in neither detinning nor iron pick-up. Therefore, the effect of this acid on the electrochemical relation between tin and iron is worthy of further study.

Later detinning accelerated by nitrate

Nitrate that has long been regarded as an accelerator of detinning, undoubtedly acted as a detinning accelerator in the present model tests. It is apparently not an initiator of detinning, because nitrate itself in the NaCl solution did not cause appreciable detinning at any *p*H tested. Furthermore, it is obvious that the co-existence of nitrate with acetic or phytic acid in the NaCl solution did not alter the electrochemical relation between tin and iron, since the extents of detinning and iron pick-up were not much changed by the addition of nitrate. However, it showed remarkable acceleration of the later detinning if the initial detinning had been caused by citric, malic, or the mixed acids. This is why we propose to divide the detinning in NaCl solutions into two stages, the initial detinning and the later detinning. Probably due to the antagonistic effect of acetic acid to citric or malic acid on the electrochemical relation between tin and iron in the NaCl solution, the nitrate-acceleration of the later detinning was less remarkable when the initial detinning was caused by the mixed acids containing acetic acid, than by citric acid alone.

Nitrate is an accelerator of detinning because it can act as a cathodic depolarizer by withdrawing electrons from the cathodic iron, and thus rendering the system unable to reach an electrochemical equilibrium. Although nitrite, nitrogen oxides, nitrogen, hydroxylamine and ammonia have been reported as the products of nitrate reduction in acidic solutions in tin cans[20,31], no appreciable amounts of nitrite or nitrogen oxides can be detected because they are excellent oxidizing reagents, and hence rapidly react with tin under acid conditions, resulting in further detinning[20,31]. In the present studies only the decrease of nitrate concentration was measured, but the reduction products were not analyzed This probably is the reason why we could not figure out a proportional relationship between the extent of detinning and the decrease in nitrate concentration, although it is distinct in each series of experiments in Table 3 that more detinning accompanied more decrease in nitrate concentration.

There are two other phenomena in connection to the effect of added nitrate worthy of mention. First, the iron pick-up that was caused by acetic acid, was not accelerated by the added nitrate at all (Table 2). Second, when nitrate was present together with a low concentration (0.01*N*) of phytic acid in the NaCl solution, both the decrease of nitrate and the extents of detinning and iron pick-up were minute, However, when nitrate was present together with a higher concentration (0.05*N*) of phytic acid, a steady decrease in nitrate concentration accompanying slight detinning at a later stage was observed. More studies on the effects of phytic acid upon detinning, iron pick-up and nitrate reduction may bring us more



valuable informations.

## Conclusion

It is concluded from the experimental results and the above discussion that,

(a) The phenomenon of detinning in NaCl solutions is likely to be divided into two stages, "initial" detinning and "later" detinning.

(b) In NaCl solutions, the initial detinning can be caused by citric or malic acid, and probably by some other compounds also, but not by nitrate.

(c) Whenever initial detinning is caused by acids or some other compounds, the later detinning can be accelerated by suitable depolarizers, which otherwise can do nothing on detinning.

(d) In NaCl solutions, if the initial detinning was caused by citric, malic or the mixed acids, nitrate can act as a good accelerator of the later detinning.

(e) Many other compounds, such as acetic and phytic acids, may exert some unexpected effects on the detinning phenomenon, and thus make the detinning mechanism more complicated.

(f) It is supposed from the results of the present studies that, in canned asparagus, citric and malic acids are responsible, at least in part, for the initial detinning, and that the later detinning is accelerated by nitrate and probably, some other depolarizers.

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## 中 文 摘 要

爲研究可能影響蘆筍罐頭脫錫的因素而進行本模擬裝罐試驗。對不同 pH 的食鹽溶液，單獨或混合添加各種有機酸與硝酸鹽，裝罐後貯藏於 45°C 下，在 40 天貯藏期間舉行定期開罐試驗。在所試有機酸中，只有檸檬酸與蘋果酸引起大量〃初期〃脫錫，硝酸鹽單獨存在時雖不能引起脫錫，但如與檸檬酸或蘋果酸共存，則可促進〃後期〃脫錫。如此，脫錫似可分爲〃初期〃脫錫與〃後期〃脫錫。但是，含有醋酸與植酸（phytic acid）的混合酸，却對脫錫表現抑阻作用。在含有硝酸鹽的鹽液繼續引起大量脫錫時，硝酸鹽濃度必逐漸減少，而 pH 則逐漸上昇。又無論有無硝酸鹽存在，只要有相當的脫錫進行，則很少有溶鐵現象。以上的實驗結果暗示，在蘆筍罐內檸檬酸與蘋果酸可能引起初期脫錫，而其後期脫錫則可能由硝酸鹽來促進。